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Formaldehyde Production in Photochemical Smog as Predicted
By Three State-of-the-Science Chemical Oxidant Mechanisms

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Formaldehyde Production in Photochemical Smog as Predicted by Three State-of-the-Science Chemical Oxidant Mechanisms

MARCIA C. DODGE

*Atmospheric Research and Exposure Assessment Laboratory, U.S. Environmental Protection Agency
Research Triangle Park, North Carolina*

A moving box model was used to compare formaldehyde (HCHO) predictions obtained with three photochemical oxidant mechanisms. In simulations using a typical urban mix of organic pollutants, the mechanisms were found to yield HCHO predictions that agreed to within 10% of each other provided the same reaction rates were used in all three mechanisms to describe the photolysis of HCHO. The agreement for simulations using pollutant mixtures containing only one organic species showed more variability. Formaldehyde predictions obtained for ethene, propene, and acetaldehyde were in excellent agreement under most conditions; significant differences, however, were noted for the 2-alkenes and aromatic hydrocarbons. Predictions of ozone and hydrogen peroxide obtained with the urban mixture were very sensitive to the initial concentration of HCHO included in the simulations. Depending on whether HCHO was assumed to constitute 0% or 2% of the initial mix of organic pollutants, resulting ozone yields varied by as much as 15-30%; hydrogen peroxide yields differed by factors of 4-10 depending on the mechanism used. To estimate the effectiveness of various control measures for limiting HCHO production, simulations were also conducted where individual organic species within the urban mix were reduced and the resulting decreases in HCHO yields were noted. The largest decreases in HCHO occurred for reductions in ethene and the other 1-alkenes; the smallest decreases were obtained when the monoalkylbenzenes or the alkanes were reduced.

INTRODUCTION

In a previous study [Dodge, 1989], oxidant predictions obtained with three recently developed mechanisms were compared for a range of volatile organic compounds (VOC) and oxides of nitrogen (NO_x) levels and for several scenarios representative of both urban and rural conditions. The mechanisms were found to yield nearly identical results for ozone, peroxyacetyl nitrate, and nitric acid under most conditions although differences were noted at (1) high NO_x concentrations, (2) high levels of aromatic hydrocarbons, and (3) low temperatures. Predictions of hydrogen peroxide were found to be in good agreement except at high VOC/NO_x ratios. In that study, little attention was paid to predictions of formaldehyde (HCHO) obtained with the mechanisms. Formaldehyde, however, is an important ingredient in photochemical smog for a number of reasons:

1. It is one of the few species that is both emitted directly into the atmosphere from combustion sources and also is produced in the atmosphere during the photodegradation of most organic species [National Research Council, 1981].
2. It is highly reactive; photolysis of HCHO produces free radicals that oxidize NO to NO₂. These same radicals also oxidize hydrocarbons to produce more formaldehyde that can contribute to ozone formation. The radicals liberated during HCHO photolysis can also react to form hydrogen peroxide (H₂O₂). In cloudwater, H₂O₂ is the major oxidizer of sulfur dioxide and, hence, it plays a significant role in acidic deposition [Penkett, et al., 1979].
3. In addition to its role in oxidant formation, HCHO is a potentially toxic air pollutant. In humans, exposure to high levels of HCHO results in irritation of the eyes and the upper respiratory system [National Research Council, 1981]; it also has

been found to be carcinogenic in animals and may be a human carcinogen as well [Clary, et al., 1983; Gibson, 1983].

Despite the fact that all current photochemical oxidant mechanisms treat the chemistry of formaldehyde, uncertainty still exists regarding the role of HCHO in urban pollution. Part of this uncertainty is due to the fact that HCHO emission sources are not well defined. Formaldehyde is known to be emitted during combustion, but the levels are poorly characterized and existing emission inventories do not report aldehydes. There is also a paucity of ambient aldehyde data due to difficulties in measuring HCHO and other aldehydes. A third uncertainty arises because HCHO production from the oxidation of hydrocarbon species is not well defined. Again, this is in part due to difficulty in obtaining reliable HCHO data and in part due to the fact that HCHO in smog systems is both produced and consumed through chemical reactions. Most of the data on HCHO production and decay are acquired in smog chamber irradiations of VOC-NO_x mixtures. Even in those laboratories where state-of-the-science analytical methods are used, the HCHO data are less accurate and reproducible than the data obtained for many other photochemical oxidants such as ozone.

Another area of uncertainty is the photochemistry of HCHO. Formaldehyde photolyzes to produce free radicals and stable products:



The rate at which HCHO photolyzes to yield these products is uncertain. Photolysis rates are determined using the expression

$$J_n = \int_{\lambda_1}^{\lambda_2} I(\lambda) \sigma_n(\lambda) \Phi_n(\lambda) d\lambda$$

where J_n is the photolysis rate for the n th photolytic process, I is the solar actinic flux at a particular location in the

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atmosphere, and σ_n and Φ_n are the absorption cross section and quantum yield, respectively, for the n th photolytic reaction. The absorption cross sections and quantum yields for HCHO have been reported by several investigators. Although the quantum yield determinations are in good agreement, the two groups of investigators who measured high-resolution absorption cross sections for HCHO [Bass *et al.*, 1980; Moortgat *et al.*, 1980] obtained values that differ by ~30% over much of the solar spectrum where HCHO absorbs. Consequently, photolysis rates calculated for HCHO are subject to some uncertainty.

The primary goal of this study was to assess how uncertainties in our understanding of HCHO emission sources and chemical reactions affect predictions obtained with state-of-the-science oxidant mechanisms. Towards that end, simulations were conducted to determine the effect of ill-defined HCHO emission levels and photolysis rates on predictions obtained for a representative mix of urban pollutants. Simulations were also conducted to investigate formaldehyde production from selected VOCs in an effort to rank organics in terms of their HCHO-forming potential. Finally, to determine the effectiveness of various VOC control measures in limiting HCHO production, simulations were performed where individual organic species within the urban mix were reduced and the resulting decreases in HCHO yields were noted.

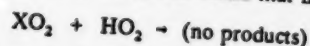
DESCRIPTION OF THE MECHANISMS

A complete description of the mechanisms is presented in Dodge [1989], and only a brief overview will be given here. The general characteristics of the mechanisms are summarized in Table 1. The Carbon Bond Mechanism - Version IV (CB4) is a "lumped structure" mechanism where organics are grouped according to the type and number of carbon bonds in each species. For example, all single-bonded carbon atoms, regardless of the molecule in which they appear, are represented by a one carbon atom alkane surrogate (called PAR), and most carbon-carbon double bonds are represented by a two carbon atom surrogate (denoted as OLE). Thus, in the carbon-bond formulation a molecule such as propene, which contains one alkyl group and one carbon-carbon double bond group, is represented as 1 PAR and 1 OLE. A species such as n -butane, which contains four alkyl groups, is represented as 4 PAR.

In contrast to the carbon-bond approach, the developers of the other two mechanisms listed in Table 1 adopted a "lumped molecule" approach in which a particular organic molecule (or a generalized organic species) is used to represent similar

organics. The CAL, which is named after its developers (Carter, Atkinson and Lurmann), is by-and-large a surrogate species mechanism. For example, the CAL contains explicit chemistry for *trans*-2-butene and that chemistry is used to describe the reactions of all 2-alkenes. The RADM mechanism, so-called because it was developed for use in the Regional Acid Deposition Model [Chang *et al.*, 1987], is best described as a lumped, parameterized species is used to represent 2-alkenes. The rate constants and products assumed for reactions of this generalized species are the average of those for the mix of highly reactive alkenes that is emitted into the atmosphere.

The version of the CB4 mechanism used in this work is identical to that used in the previous analysis [Dodge, 1989] with one exception. In the previous study, it was found that the CB4 generated extremely high yields of H_2O_2 at high VOC/ NO_x ratios due to the treatment of alkylperoxy radicals in the mechanism. Most alkylperoxy radicals have been replaced in the CB4 with an operator, called XO_2 , that converts NO to NO_2 . The only loss processes included for XO_2 were reactions with NO and with itself. No reaction of XO_2 with HO_2 was included in the CB4 although such a reaction can be important at low NO concentrations. It was found that if the reaction



was added to the mechanism with a rate constant of $9 \times 10^3 \text{ ppm}^{-1} \text{ min}^{-1}$ (as recommended by DeMore *et al.* [1987] for the reaction of CH_3O_2 with HO_2), predictions of H_2O_2 obtained at high VOC/ NO_x ratios decreased substantially and were brought into closer agreement with the values predicted by the CAL and RADM. Hence, this reaction is included in the CB4 mechanism used in the present work.

The CAL mechanism used in this study is identical to the version used in the previous work. The RADM mechanism, however, is a revised version of the one previously used. In the Dodge [1989] analysis, it was found that O_3 yields obtained with the RADM, when simulating VOC mixtures that contained only aromatic hydrocarbons, exceeded those of the other two mechanisms by a significant amount. The high O_3 predictions were due to the chemistry assumed for the OH oxidation pathway that leads to fragmentation of the aromatic ring. Less than 50% of the products formed in this ring-cleavage process have been identified in laboratory studies. The RADM developers originally used highly reactive dicarbonyl species to represent the unidentified products. After the Dodge [1989] study, the RADM mechanism was tested against a large data base of smog chamber experiments [Carter and Lurmann, 1990]. The results of that evaluation also indicated that the RADM aromatics mechanism was too reactive, due to the use of dicarbonyls as surrogates for the unknown reaction products. As a result, the RADM developers revised their aromatics chemistry; dicarbonyl yields in the new mechanism are now comparable to those observed in laboratory studies of aromatic hydrocarbons. Several other changes were also made to the mechanism, including a general updating of rate constants and some revisions in the manner used to assign VOC species to the generalized species contained in the mechanism. The version of RADM used in the present work is the one referred to as "RADM-P" in the Carter and Lurmann [1990] evaluation.

DESCRIPTION OF THE MODELING APPROACH

All simulations were conducted with the OZIPM-4 moving box model developed by Hogo and Gery [1988]. The inputs used in the model were designed to represent a typical urban

TABLE 1. Mechanisms Used in the Study

Mechanism	Type ^a	Reactions ^b	Species ^c	Primary VOCs ^d
CB4 [Gery <i>et al.</i> , 1988; 1989]	LS	81	34	9
CAL [Carter <i>et al.</i> , 1986] [Lurmann <i>et al.</i> , 1987]	LM	132	51	12
RADM [Stockwell <i>et al.</i> , 1990]	LM	157	57	13

^aLS, lumped structure; LM, lumped molecule.

^bNumber of reactions included in the mechanism.

^cNumber of species included in the mechanism.

^dNumber of organic species for which either emissions or initial conditions should be specified.

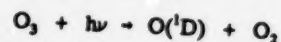
pollution episode and are summarized in Table 2. Calculations were carried out from 0800 to 2000 local daylight time using diurnally varying temperature and solar radiation profiles. The simulations were commenced assuming initial concentrations of VOC, NO_x, and CO. For the base case simulations, [VOC]_i and [NO_x]_i were taken to be 0.54 ppm C and 0.06 ppm, respectively, for a VOC/NO_x ratio of 9:1. Simulations were also conducted where [VOC]_i was varied from a low of 0.27 ppm C to a high of 1.08 ppm C, corresponding to VOC/NO_x ratios ranging from 4.5:1 to 18:1. Emissions of VOC, NO_x, and CO were added to the box as it moved along its trajectory with the largest fractions added during the first several hours of the simulations. The height of the box was allowed to increase during the morning hours to account for the breakup of the nocturnal inversion layer. As the mixing height increased, VOC, O₃, and CO were entrained into the box from aloft at the concentrations specified in Table 2.

TABLE 2. Simulation Conditions

Parameter	Definition
Location	Philadelphia, Pa.
Solar radiation	determined for clear-sky conditions on July 15
Temperature	varied from a morning low of 20°C to an afternoon high of 30°C
Simulation period	0800 to 2000 local daylight time
Initial concentrations	variable for [VOC] _i [NO _x] _i = 0.06 ppm [NO ₂] _i = 25% [NO _x] _i [CO] _i = 1.2 ppm [H ₂ O] _i = 20,000 ppm
Emissions	temporally varying emissions of VOC, NO _x , and CO added
Mixing height	increased from 300 m to 1300 m
Concentrations aloft	[VOC] = 0.025 ppm C [O ₃] = 0.05 ppm [CO] = 0.5 ppm
Dry deposition	included for O ₃ , H ₂ O ₂ , NO ₂ , HNO ₃ , and PAN

The photolysis rates used for NO₂ in the model simulations were derived using the JSPECTRA program developed by Jeffries *et al.* [1989a] and the absorption cross sections and quantum yields recommended for NO₂ by the NASA Data Evaluation Panel [DeMore *et al.*, 1987]. The JSPECTRA program uses a radiative transfer model developed by the authors to calculate solar actinic flux as a function of column O₃, water vapor, and aerosol scattering and absorption. For the simulations conducted in this study, typical eastern U.S. summertime, clear-sky atmospheric conditions were assumed. The absorption cross sections and quantum yields used for NO₂ had a 2-nm wavelength resolution. Following the OZIPM-4 guidelines [Hogo and Gery, 1988], photolysis rate constants were calculated for an altitude of 640 m. This altitude represents the daytime average of the mixed layer for most urban areas. With two exceptions, the rate constants used for the other photolysis reactions were the ratios to the NO₂ photolysis rate rec-

ommended by each of the mechanism developers for solar zenith angles between 0° and 86°. The two exceptions were the photolysis of O₃ to singlet oxygen,



and the photolysis of HCHO. Jeffries and Sexton [1987] showed that photolysis rates for these reactions do not vary with altitude in the same manner as NO₂. Therefore, the JSPECTRA program and the absorption cross sections and quantum yields recommended for use with the CB4 mechanism [Gery *et al.*, 1988] were employed to calculate photolysis rates for O₃ at 640 m. These absorption cross sections and quantum yields are almost identical to those recommended for use with the RADM, but are of finer wavelength resolution than the values recommended by the developers of the CAL. The same procedure was followed to derive rate constants for the photolysis of HCHO. The quantum yields used were those recommended by Calvert [1980]. Given the uncertainty in HCHO absorption cross sections, photolysis rates were calculated using both the cross sections reported by Bass *et al.* [1980] and those determined by Moortgat *et al.* [1980]. The effect of using these different HCHO cross sections on predictions obtained with the mechanisms will be described in a later section.

The compositions used in this study for the surface-layer VOCs and the VOCs entrained from aloft are provided in Table 3. The fractions given for the CB4 and CAL were derived by Jeffries *et al.* [1989b] from an analysis of VOC data collected within and aloft of selected urban areas. This same ambient data base was also analyzed in the present work to derive the carbon fractions shown in Table 3 for the new RADM mechanism. These carbon fractions differ from those used in the Dodge [1989] study with the older version of the RADM mechanism because, following the recommendations of the RADM developers, several organic species have been reassigned to different model species in the new mechanism.

Organic species in the RADM are weighted according to their reactivity when assigned to their surrogate classes. That is, the individual organics are weighted by the ratio of their reaction rate with OH to that of the surrogate species. In most cases the OH rate constants for the individual species are very similar to the rate constants for the surrogate species. Hence, in deriving carbon fractions for the RADM, the only species weighted for their OH reactivity were propane, acetylene, and benzene.

Note that in many cases the carbon fractions for the three mechanisms are different even for those surrogates that are common to all mechanisms. This occurred because the techniques used to assign individual VOCs to their model representatives are not the same in all mechanisms. For example, the HCHO and ALD2 surrogate fractions are larger in the CB4 than in the other mechanisms because the CB4 developers use these surrogates to represent some non-aldehyde organics. Most notably, the ALD2 fraction is high in the CB4 because ALD2 in that mechanism is used as a surrogate for 2-alkenes on the assumption that 2-alkenes react so readily to form aldehydes that they can be represented by their aldehyde products.

The data used to derive the carbon fractions given in Table 3 for the surface layer did not include measurements of aldehydes. Jeffries *et al.* [1989b] assumed a total aldehyde content of 5%, apportioned as 2% HCHO and 3% acetaldehyde. The effect of assuming different levels of initial aldehydes on oxidant predictions will be described in a subsequent section.

TABLE 3. Carbon Fractions Used to Apportion VOC in the Surface Layer and Aloft into the Organic Surrogates Used in Each Mechanism

CB4			CAL			RADM		
Species ^a	Surface	Aloft	Species ^b	Surface	Aloft	Species ^c	Surface	Aloft
PAR	0.564	0.498	ALK4	0.214	0.363	ETHA	0.042	0.222
			ALK7	0.280	0.151	HC3	0.107	0.194
						HCS	0.142	0.118
						HC7	0.147	0.037
ETH	0.037	0.034	ETHE	0.037	0.034	OL2	0.037	0.034
OLE	0.035	0.020	PRPE	0.050	0.020	OLT	0.058	0.023
			TBUT	0.026	—	OLI	0.032	—
TOL	0.089	0.042	TOLU	0.080	0.042	TOL	0.089	0.051
XYL	0.117	0.026	XYLE	0.079	0.026	XYL	0.135	0.029
			TMBZ	0.042	—			
HCHO	0.021	0.070	HCHO	0.020	0.070	HCHO	0.020	0.070
ALD2	0.052	0.037	ALD2	0.030	0.037	ALD	0.030	0.037
			RCHO	—	—			
NR	0.085	0.273	NR	0.142	0.257	NR	0.161	0.185

^aPAR, single-carbon bond; ETH, ethene; OLE, carbon-carbon double bond; TOL, toluene; XYL, xylene; HCHO, formaldehyde; ALD2, acetaldehyde; NR, nonreactive carbon.

^bALK4, C₄-C₅ alkanes; ALK7, C₆+ alkanes; ETHE, ethene; PRPE, propene; TBUT, *trans*-2-butene; TOLU, toluene; XYLE, xylene; TMBZ, trimethylbenzene; HCHO, formaldehyde; ALD2, acetaldehyde; RCHO, C₃+ aldehydes; NR, nonreactive carbon.

^cETHA: ethane; HC3, acetylene and C₃-C₄ alkanes; HCS, C₅-C₆ alkanes; HC7, C₆+ cycloparaffins and C₇+ alkanes; OL2, ethene; OLT, 1-alkenes; OLI, 2-alkenes and dienes; TOL, monoalkylbenzenes; XYL, di- and trialkylbenzenes; HCHO, formaldehyde; ALD, acetaldehyde; NR, nonreactive carbon.

SIMULATION RESULTS

Effect of HCHO Photolysis Rates on Predictions

The conditions specified in Tables 2 and 3 were first used to investigate the effect of uncertainties in the rate of HCHO photolysis on predictions obtained with the three mechanisms. As noted previously, two sets of high-resolution absorption cross section data have been reported for HCHO [Bass *et al.*, 1980; Moortgat *et al.*, 1980]. The CB4 developers, in their mechanism evaluation study, calculated photolysis rates for HCHO using 1-nm values of the cross sections reported by Bass *et al.* [1980]. The CAL developers followed the recommendations of the NASA Data Evaluation Panel [DeMore *et al.*, 1987] and used 10 nm-resolved averages of the cross sections measured by Bass *et al.* [1980] and Moortgat *et al.* [1980]. The RADM developers used 1-nm averages of the Bass and Moortgat data. As a result of these choices, the recommended rate of photolysis of HCHO to free radicals is approximately 15-20% lower in the CB4 than in the CAL and RADM mechanisms where the calculated rates agree to within 4%.

To determine what effect uncertainties in HCHO photolysis rates have on predictions, formaldehyde photolysis rates were first calculated using the cross sections measured by Bass *et al.* [1980] and then the cross sections determined by Moortgat *et al.* [1980]. A third set of calculations was also performed using the 1 nm-resolved averages of the Bass and Moortgat data. The results obtained are given in Table 4. Note that O₃ predictions were not greatly affected by the choice of HCHO photolysis rates. Depending on the mechanism used, predictions of maximum O₃ concentrations varied by only 3-5%. The different HCHO photolysis rates, however, caused H₂O₂ predictions to vary by 30-50%.

The HCHO profiles obtained when either the Bass or the Moortgat absorption cross sections were used to calculate photolysis rates are shown in Figure 1. Note that in the late stages of the simulation, HCHO concentrations obtained with any one mechanism differed by approximately 20% depending on which set of photolysis rates was used. For example, at the end of the simulation, the HCHO concentration predicted by the CB4 was 9.6 ppb when the Bass data were used; the

TABLE 4. Effect of Varying HCHO Photolysis Rates for an Urban Mix Simulation Containing 5% Initial Aldehydes

Absorption Cross Sections Used for Formaldehyde	Maximum Ozone Concentration				Maximum H ₂ O ₂ Concentration			
	CB4	CAL	RADM	Δ , %	CB4	CAL	RADM	Δ , %
Bass <i>et al.</i> [1980]	161	166	163	3	0.6	1.2	0.8	70
Average ^b	167	169	167	1	0.8	1.4	1.0	55
Moortgat <i>et al.</i> [1980]	170	171	169	1	1.0	1.6	1.1	50
Difference ^a	5%	3%	4%		50%	30%	30%	

Concentrations are in ppb; [VOC]₀ = 0.54 ppm C and [NO_x] = 0.06 ppm.

^aDifference between the highest and the lowest maximum concentration relative to the mean.

^bAverage of the absorption cross sections reported by Bass *et al.* [1980] and Moortgat *et al.* [1980].

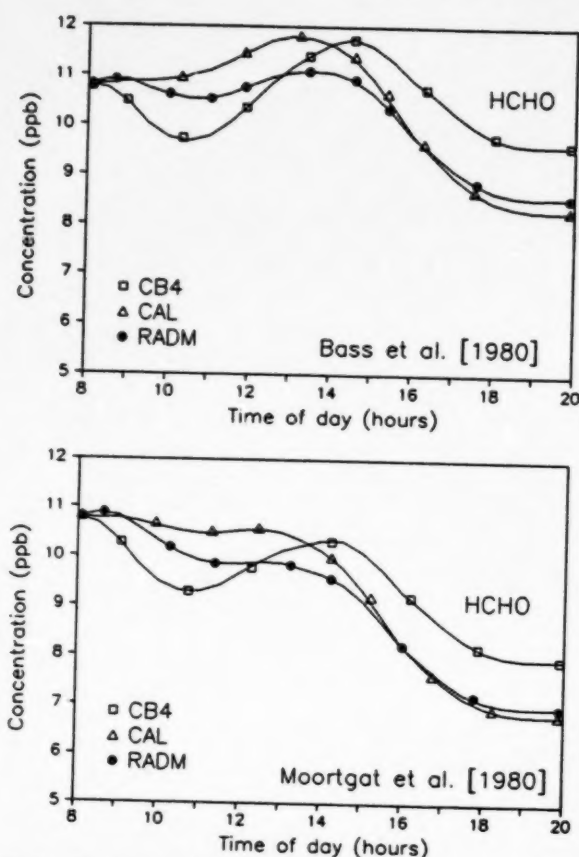


Fig. 1. Comparison of HCHO profiles obtained using the Bass *et al.* [1980] and Moortgat *et al.* [1980] absorption cross section data. (See Table 4 for initial conditions.)

concentration was 8.0 ppb when the Moortgat data were used to derive HCHO photolysis rates. When the same photolysis rates were used in all three mechanisms, the shapes of the profiles were somewhat different. The onset of HCHO formation seemed to occur most rapidly in the CAL simulations and appeared to be most delayed in the CB4 simulations. Note, however, that HCHO predictions obtained with the three mechanisms at all stages of the simulations usually agreed to within 1 ppb provided the same set of photolysis rates were used.

Because of the high initial loading of HCHO in the simulations presented in Figure 1, it is difficult to compare HCHO production in the three mechanisms. It is easier to make a comparison if HCHO is not included in the initial pollutant mix. Therefore, the simulations presented in Table 4 were repeated using an initial VOC mixture that contained no aldehydes. In these simulations, the 5% initial aldehydes included in the urban mix were removed, and the percentage of other VOCs in the mix was proportionately increased so that the remaining VOCs totalled to 100%. The resulting maximum HCHO concentrations obtained at three different VOC/NO_x ratios are given in Table 5. Depending on the choice of photolysis rates, maximum HCHO concentrations simulated with any one mechanism can vary from 9-16%. The effect of using different rates is most pronounced at low VOC/NO_x ratios. Provided the same rate constants are used in all three

TABLE 5. Effect of Varying HCHO Photolysis Rates for an Urban Mix Simulation Containing No Initial Aldehydes

Absorption Cross Sections Used for Formaldehyde	VOC/NO _x	Maximum HCHO Concentration			
		CB4	CAL	RADM	Δ, %
Bass <i>et al.</i> [1980]	6:1	5.8	6.3	5.8	8
Average ^b	6:1	5.5	5.8	5.3	9
Moortgat <i>et al.</i> [1980]	6:1	5.1	5.4	5.0	8
	Difference ^a	13%	16%	15%	
Bass <i>et al.</i> [1980]	9:1	9.4	9.4	8.7	8
Average ^b	9:1	8.9	8.8	8.2	8
Moortgat <i>et al.</i> [1980]	9:1	8.4	8.3	7.7	9
	Difference ^a	11%	12%	15%	
Bass <i>et al.</i> [1980]	18:1	17.6	16.6	15.8	11
Average ^b	18:1	16.6	15.8	14.9	11
Moortgat <i>et al.</i> [1980]	18:1	15.9	15.1	14.2	11
	Difference ^a	10%	9%	11%	

Concentration are in ppb; [NO_x]_i = 0.06 ppm.

^aDifference between the highest and the lowest maximum concentration relative to the mean.

^bAverage of the absorption cross sections reported by Bass *et al.* [1980] and Moortgat *et al.* [1980].

mechanisms, the results obtained for HCHO are in reasonably good agreement. At the low ratio, however, the CAL predicts somewhat higher levels of HCHO than the CB4 and RADM. At the higher ratios, the RADM predicts somewhat less HCHO than the other two mechanisms.

A primary purpose of this study is to compare predictions of HCHO production obtained with the three mechanisms. The results presented in Figure 1 and Table 5 clearly show that the choice of photolysis rates has a substantial effect on the rate of consumption of HCHO. Consequently, it is necessary to use the same photolysis rates for HCHO in all three mechanisms if differences in HCHO formation rates are to be isolated from differences in HCHO consumption rates. Although the choice is somewhat arbitrary, the remaining simulations presented in this study will be conducted using 1-nm averages of the absorption cross sections determined by Bass *et al.* [1980] and Moortgat *et al.* [1980].

Effect of Initial Aldehydes on Predictions

As previously mentioned, it is uncertain what fraction of the VOCs emitted into the atmosphere is composed of aldehydes. These species are not reported in emission inventories and the existing ambient data are sparse and of questionable accuracy. In deriving the carbon fractions given in Table 3, Jeffries *et al.* [1989b] assumed a total aldehyde content of 5%, apportioned as 2% HCHO and 3% acetaldehyde. Lurmann *et al.* [1987], when estimating carbon fractions for use with the CAL, also assumed 5% although they apportioned it as 3% HCHO and 2% acetaldehyde. Their values were based on aldehyde data collected in Los Angeles although Lurmann *et al.* indicated that the 5% estimate was probably an upper limit.

To examine the effect of aldehyde emission levels on predictions, a series of simulations was carried out using initial aldehyde concentrations that comprised from 0% to 5% of the urban mix. The results obtained at a VOC/NO_x ratio of 9:1 are reported in Table 6. The concentrations of initial VOC and the added VOC emissions were the same in all these simulations. Thus, when aldehydes were subtracted, other VOCs were added in proportion to the amounts given in Table 3 to

TABLE 6. Effect of Initial Aldehyde Concentration on Predictions of Ozone and Hydrogen Peroxide

[Formaldehyde] _i	[Acetaldehyde] _i	Maximum Ozone Concentration				Maximum H ₂ O ₂ Concentration			
		CB4	CAL	RADM	Δ, %	CB4	CAL	RADM	Δ, %
3%	2%	172	172	171	<1	1.2	1.8	1.2	43
2%	3%	167	169	167	1	0.8	1.4	1.0	55
2%	—	155	162	160	4	0.5	1.1	0.7	75
1%	1%	144	158	153	9	0.3	0.8	0.5	100
—	3%	134	153	146	13	0.2	0.6	0.8	120
—	—	115	142	135	21	0.05	0.3	0.2	125
Difference		40%	20%	25%		200%	150%	150%	

Concentrations are in ppb; [VOC]_i = 0.54 ppm C and [NO_x]_i = 0.06 ppm.

*Difference between the highest and the lowest maximum concentration relative to the mean.

make up the difference. As noted in Table 6, there is a significant difference in the predicted maximum O₃ and H₂O₂ concentrations depending on the amount and make-up of the aldehydes included in the VOC mix. The magnitude of the effect depends critically on the VOC/NO_x ratio of the mixture being simulated. The effect is most pronounced at low VOC/NO_x; at high ratios, predicted O₃ and H₂O₂ concentrations show much smaller variations with changes in initial aldehyde concentration. For example, as shown in Table 6, O₃ predictions obtained with the RADM at a VOC/NO_x ratio of 9:1 varied by 25% depending on the level of aldehydes included in the mix. At a ratio of 6:1, the difference increased to 35%; at a ratio of 18:1 there was only a 5% difference in O₃ predictions depending on whether aldehydes were assumed to constitute 0% or 5% of the initial mix. These results are in agreement with those obtained in an earlier modeling study [Dodge, 1984] where the O₃-forming potential of various organic constituents in an urban-like VOC mix was compared. In that study it was found that different organic species displayed significantly different O₃-forming potentials at low VOC/NO_x ratios, but comparable O₃-forming potentials at high ratios.

At all VOC/NO_x ratios investigated in this study, predictions of O₃ and H₂O₂ obtained with the CB4 were found to be the most sensitive to the initial aldehyde concentration, and predictions obtained with the CAL showed the least sensitivity. Even when the CAL mechanism was used, however, O₃ predictions obtained at low and moderate VOC/NO_x ratios differed by at least 20%, and peak H₂O₂ concentrations varied by factors of 6 or more; hence, accurate characterization of aldehyde emissions is critical if O₃ and H₂O₂ formation in the urban environment is to be predicted reliably.

Note in Table 6 that the predictions of the mechanisms agreed most closely when the aldehyde loading was high. The reason for this is that the three mechanisms have different induction periods. The onset of O₃ formation under most conditions occurs most rapidly in the CAL simulations and most slowly in the CB4 simulations. The mechanisms, however, generally are in close agreement if the full oxidizing potential of the mixture being simulated is reached prior to sunset. In the mixtures containing low initial concentrations of aldehydes, sunset occurs before the maximum oxidant-forming potential has been attained and more of a discrepancy in O₃ and H₂O₂ levels is observed. This difference in induction periods is demonstrated in Figure 2 where concentration-time profiles are shown for the simulation containing no initial aldehydes. Note that the onset of O₃, HCHO, and H₂O₂ production occurred most rapidly in the CAL simulation and was most delayed in the CB4 simulation. Formaldehyde production in the CB4, however, accelerated in the later stages of the simulation, with

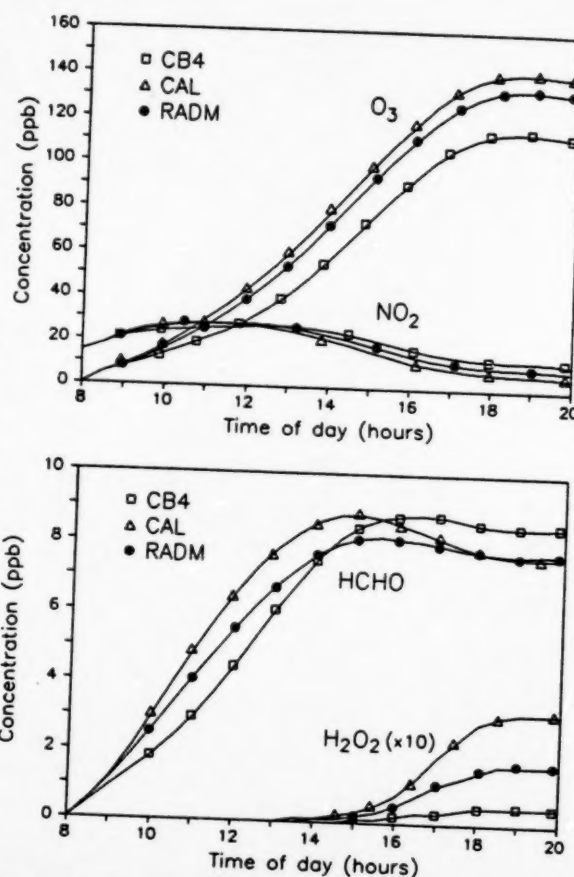


Fig. 2. Predicted oxidant concentrations as a function of time for the urban mix simulation containing no initial aldehydes; VOC/NO_x = 9:1.

the result that the maximum HCHO concentration obtained with the CB4 was somewhat higher than that predicted by the RADM but nearly identical to that obtained with the CAL.

Formaldehyde Production from Oxidation of Selected VOCs

To determine the relative contribution of various organics to the net production of HCHO, a series of simulations was conducted using VOC mixtures that contained only one organic species. The initial conditions for these simulations were the same as given in Table 2 except that there was no entrainment of VOC or O₃ from aloft as the mixing height increased. The net production of HCHO from eight different organics was

TABLE 7. Comparison of Results Obtained for Selected VOC Species at a VOC/NO_x Ratio of 9:1

VOC Species	Maximum HCHO Concentration					Maximum O ₃ Concentration					Maximum H ₂ O ₂ Concentration				
	CB4	CAL	RADM	Mean	Δ, %	CB4	CAL	RADM	Mean	Δ, %	CB4	CAL	RADM	Mean	Δ, %
Formaldehyde	—	—	—	—	—	225	222	219	222	3	13	13	13	13	0
Ethene	62	65	67	65	8	285	281	274	280	4	15	15	13	14	14
Propene	52	49	51	51	6	256	238	237	244	8	18	13	11	14	50
<i>trans</i> -2-Butene	30	23	34	29	38	230	217	221	223	6	10	10	8	9	22
Acetaldehyde	30	27	28	28	11	230	208	209	216	10	10	7	5	7	70
Trimethylbenzene	9	8	4	7	70	190	190	203	194	7	8	9	5	7	60
Xylene	9	6	4	6	80	191	178	206	192	15	9	8	6	7	40
Toluene	3	4	3	3	30	22	83	112	72	125	—	—	—	—	—
Alkane mix ^b	<1	<1	<1	<1	—	2	3	2	2	50	—	—	—	—	—
Urban mix ^c	8.9	8.8	8.2	8.6	8	115	142	135	131	21	0.05	0.3	0.2	0.2	125

Concentrations are in ppb; [VOC]₀ = 0.54 ppm C and [NO_x]₀ = 0.06 ppm.

^aDifference between the highest and the lowest maximum concentration relative to the mean.

^bBased on alkane carbon fractions given in Table 3.

^cNo initial aldehydes.

investigated, and the results obtained at a VOC/NO_x ratio of 9:1 are presented in Table 7. For comparison purposes, the results of the urban mix simulation shown in Figure 2 are included. A formaldehyde-only VOC mixture was also simulated to determine if the mechanisms are comparable in their treatment of formaldehyde chemistry. As noted in Table 7, predictions of O₃ and H₂O₂ obtained in the HCHO simulation are in excellent agreement for all mechanisms. This is not surprising since the chemistry for the inorganic species is very comparable in the three mechanisms; likewise, since the same photolytic rate constants were used for HCHO, formaldehyde chemistry is also nearly identical in all mechanisms.

In conducting the simulations for the eight HCHO-producing organics, the rate constants for some of the VOC species included in the RADM mechanism were altered. As mentioned previously, the RADM uses generalized species to represent most organics. In the case of organics such as propene, *trans*-2-butene and the aromatic VOCs, the rate constants and products assumed for the generalized species are not the same as those for the individual VOCs simulated in this study. The rate constants for these generalized species were adjusted to those of the individual organic being simulated; no change, however, was made to any of the reaction products in the mechanism. A similar change in rate constants was not made to the CAL mechanism since the specific organics investigated in this study are all represented explicitly in that mechanism.

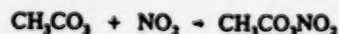
The individual VOCs listed in Table 7 are ranked in descending order of their ability to produce formaldehyde with ethene, the largest producer, at the top and the alkane mix, which produced the least HCHO, at the bottom. Note that this is also the order for production of O₃ and H₂O₂. Thus, organics that produce high HCHO yields also tend to produce high levels of O₃ and H₂O₂.

Concentration-time profiles of oxidant formation are shown in Figure 3 for the three alkenes investigated in this study. Note that excellent agreement among the mechanisms was achieved for the ethene simulation. In the case of propene, the HCHO profiles were nearly identical for all three mechanisms. The CB4, however, generated somewhat higher levels of O₃ and H₂O₂ than the CAL and RADM.

The agreement achieved for the *trans*-2-butene simulation is not as good. In the CB4, one mole of *trans*-2-butene is represented as two moles of acetaldehyde. Because of the

lower initial reactivity of acetaldehyde compared to *trans*-2-butene, the onset of O₃ formation occurs later in the CB4 simulation although comparable peak levels are obtained for all three mechanisms. The shapes of the HCHO profiles are also quite different for each mechanism. Most of the difference between the CB4 and CAL profiles can be attributed to the use of acetaldehyde as a surrogate for *trans*-2-butene in the CB4. The difference between the CAL and RADM formaldehyde profiles also is largely due to the different representation of 2-alkenes in those mechanisms. The CAL contains explicit chemistry for *trans*-2-butene, and that chemistry is used to represent all the 2-alkenes and other highly reactive alkenes such as the dienes. In the RADM, the 2-alkenes and the dienes are represented using a generalized species; the products assumed for reactions of this generalized species are the average of those for a typical urban mixture of highly reactive alkenes. Dienes react with OH to liberate HCHO whereas the 2-alkenes form only acetaldehyde and higher aldehydes on initial attack by OH. Thus, HCHO is included as a reaction product in the RADM mechanism whereas the only aldehyde product included for reaction of the 2-alkene CAL surrogate is acetaldehyde. Therefore, most of the rapid, initial formation of HCHO in the RADM is an artifact resulting from the use of a generalized species to represent *trans*-2-butene. It is interesting to note, however, that despite the differences in the shapes of the three HCHO profiles, formaldehyde concentrations integrated over the 12-hour simulation period appear to be quite comparable for all three mechanisms.

The results obtained for the acetaldehyde simulation are depicted in Figure 4. (The profiles shown for the CB4 are identical to those shown in the previous figure for *trans*-2-butene since acetaldehyde in the CB4 is used as a surrogate for 2-alkenes.) Note that maximum O₃ and HCHO concentrations simulated with the CB4 are approximately 10% higher than those obtained with the CAL and RADM. Acetaldehyde chemistry in the three mechanisms is nearly identical except for the treatment of peroxyacetyl nitrate (PAN) chemistry. As discussed in Dodge [1989], the CB4 developers assume a large negative activation energy for the reaction of peroxyacetyl radicals with NO₂.



The CAL and RADM developers, on the other hand, assume

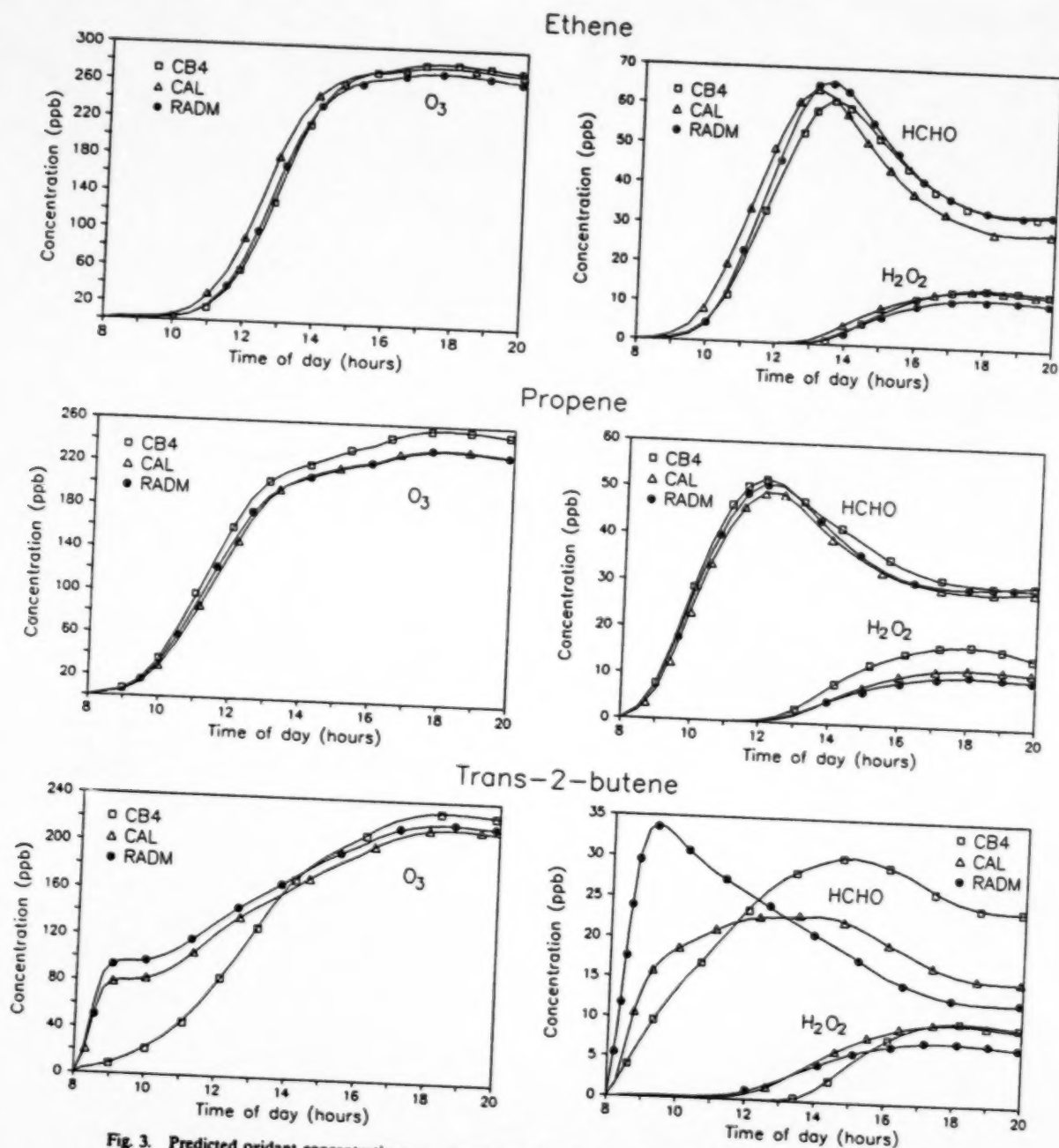


Fig. 3. Predicted oxidant concentrations as a function of time for the alkene simulations; $\text{VOC}/\text{NO}_x = 9:1$.

an activation energy for this reaction that is close to zero. The maximum temperature of this simulation was 30°C . At that temperature, PAN formation proceeds at a faster rate in the CAL and RADM than in the CB4. This has an inhibiting effect on O_3 and HCHO formation since PAN serves as a sink for free radicals and NO_2 .

If the same rate expression for the PAN-formation reaction is used in all three mechanisms, predictions obtained for the acetaldehyde simulation agree to within 1 ppb for HCHO and to within 5 ppb for O_3 . For example, when the rate expression used in the CB4 is also used in the other mechanisms, the peak HCHO concentrations obtained with the CB4, CAL, and

RADM are 30, 29, and 30 ppb, respectively; maximum O_3 concentrations are 230, 225, and 226 ppb. Similarly good agreement is achieved when the rate expression used in the CAL and RADM is also used in the CB4. Given the importance of the PAN-formation reaction on both HCHO and O_3 predictions, additional kinetic data are needed to determine which treatment of peroxyacetyl chemistry is the more valid.

The results obtained for the simulations containing aromatic VOCs are shown in Figure 5. Note that there are significant discrepancies in the HCHO yields simulated with the three mechanisms for each of the aromatic hydrocarbons. In the toluene simulation, the CAL predicted a maximum HCHO

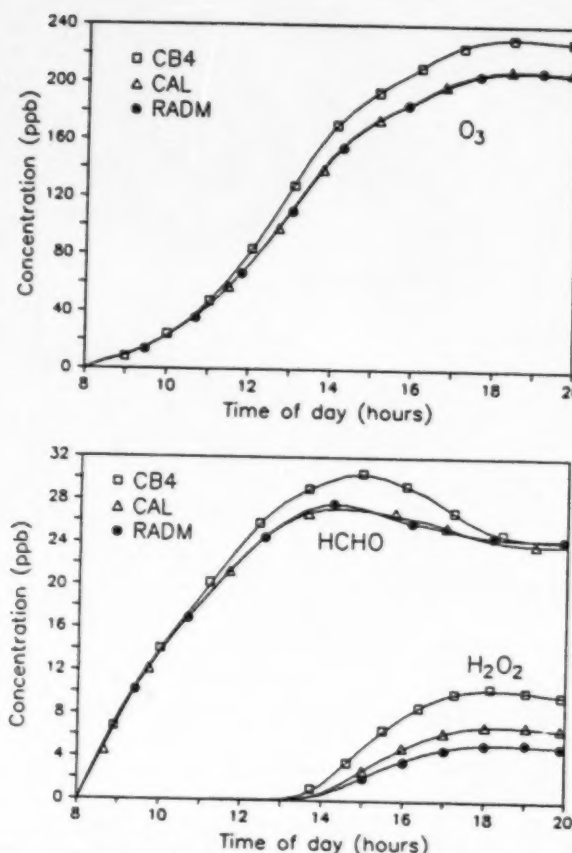
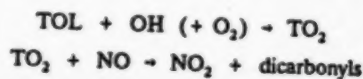


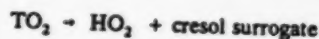
Fig. 4. Predicted oxidant concentrations as a function of time for the acetaldehyde simulation; VOC/NO_x = 9:1.

concentration that was 30% higher than that obtained with the other mechanisms although the peak concentrations for all three mechanisms were very low. In the xylene and trimethylbenzene simulations, the highest HCHO yields were obtained with the CB4, and the lowest yields were achieved with the RADM. The yields, although higher than those obtained for toluene, were still a factor of 4-10 lower than the HCHO yields achieved in the alkene and acetaldehyde simulations.

Note in Figure 5 that there is significant disagreement in the simulated O₃ yields for toluene. The chemistry of aromatic VOCs is highly uncertain. All three mechanisms assume that OH adds to toluene to form an intermediate that can react with NO to produce a variety of products including dicarbonyl species:



The CB4 developers also assume that the TO₂ adduct can rearrange:



Because the reactivity of the cresol surrogate is significantly less than the reactivity of dicarbonyl species, less O₃ results from oxidation of toluene in the CB4 than occurs in the other mechanisms.

The different treatments of toluene chemistry are largely re-

sponsible for the discrepancies noted for O₃ in the urban mix simulation shown in Figure 2. To demonstrate, the TO₂ rearrangement reaction was removed from the CB4 mechanism, and the urban mix simulation was repeated. Peak O₃ increased from 115 to 137 ppb, in much closer agreement to the yields of 142 and 135 ppb obtained with the CAL and RADM. Hydrogen peroxide predictions also increased from 0.05 to 0.15 ppb, closer to the values of 0.3 and 0.2 ppb obtained with the CAL and RADM. Formaldehyde predictions, however, increased from 8.9 to 9.6 ppb, which is 9 and 17% higher than the CAL and RADM values. This suggests that the good agreement noted for HCHO production in the urban mix simulation may be fortuitous. If the mechanisms were more comparable in their predictions of O₃ and H₂O₂, their predictions of HCHO might not agree as well.

Although this test case was conducted by altering the CB4 rather than the CAL and RADM mechanisms, there is justification to support the treatment of toluene chemistry in the CB4. In simulations of O₃ production in smog chamber studies of toluene-NO_x mixtures, predictions obtained with the CB4, on average, were within 1% of the observed yields [Gery et al., 1988]. The CAL and RADM mechanisms yielded peak O₃ concentrations that exceeded the observed levels, on average, by 11% [Lurmann, et al., 1987] and 17% [Carter and Lumann, 1990], respectively.

Ozone predictions obtained with the three mechanisms for the xylene and trimethylbenzene simulations were in better agreement. Note in Figure 5, however, that the onset of O₃ and HCHO formation occurred more rapidly in the CAL and RADM than in the CB4 simulations. The differences noted for the trimethylbenzene simulation largely result from the different lumping techniques used in the mechanisms to represent trialkylated aromatics. In the CAL these species are represented using the surrogate trimethylbenzene. In the RADM, a single generalized species is used to represent both the di- and trialkylated aromatics; in this particular simulation, the rate constant used for reaction of the generalized species with OH was adjusted to the rate constant for trimethylbenzene. In the CB4, trimethylbenzene is represented as 1 XYL + 1 PAR, where XYL and PAR are the surrogates for xylene and single-carbon bonds, respectively. Judging from the delayed onset of O₃ and HCHO formation in the CB4, the initial reactivity of the surrogates used to represent trimethylbenzene in the CB4 is less than the reactivity of the surrogate species used in the other mechanisms.

Also included in Table 7 are the results obtained for an alkane mixture where the proportion of the various alkanes in the simulation was the same as given in Table 3 for the surface-layer VOC composition. As noted in Table 7, the alkane mix was extremely unreactive and generated very low levels of oxidants. To boost the reactivity of the alkane mix so that a better comparison of HCHO predictions could be made, a second test was conducted where hydroxyl radicals were added in the simulation at a constant rate of 1×10^{-4} ppm min⁻¹. The resulting O₃ yields were in excellent agreement for the three mechanisms (150, 142, and 145 ppb). Formaldehyde predictions, however, showed significant discrepancies (7.3, 6.4, and 4.6 ppb for the CB4, CAL, and RADM). Large variations were also noted for H₂O₂ with predictions that ranged from a low of 8 ppb for the RADM to a high of 13 ppb for the CAL.

To investigate the dependence of HCHO formation on VOC levels, two additional sets of calculations were carried out using the organic mixtures presented in Table 7. In one set, the VOC concentration was decreased by a factor of 2, resulting in a VOC/NO_x ratio of 4.5:1; in the other set, VOC was increased

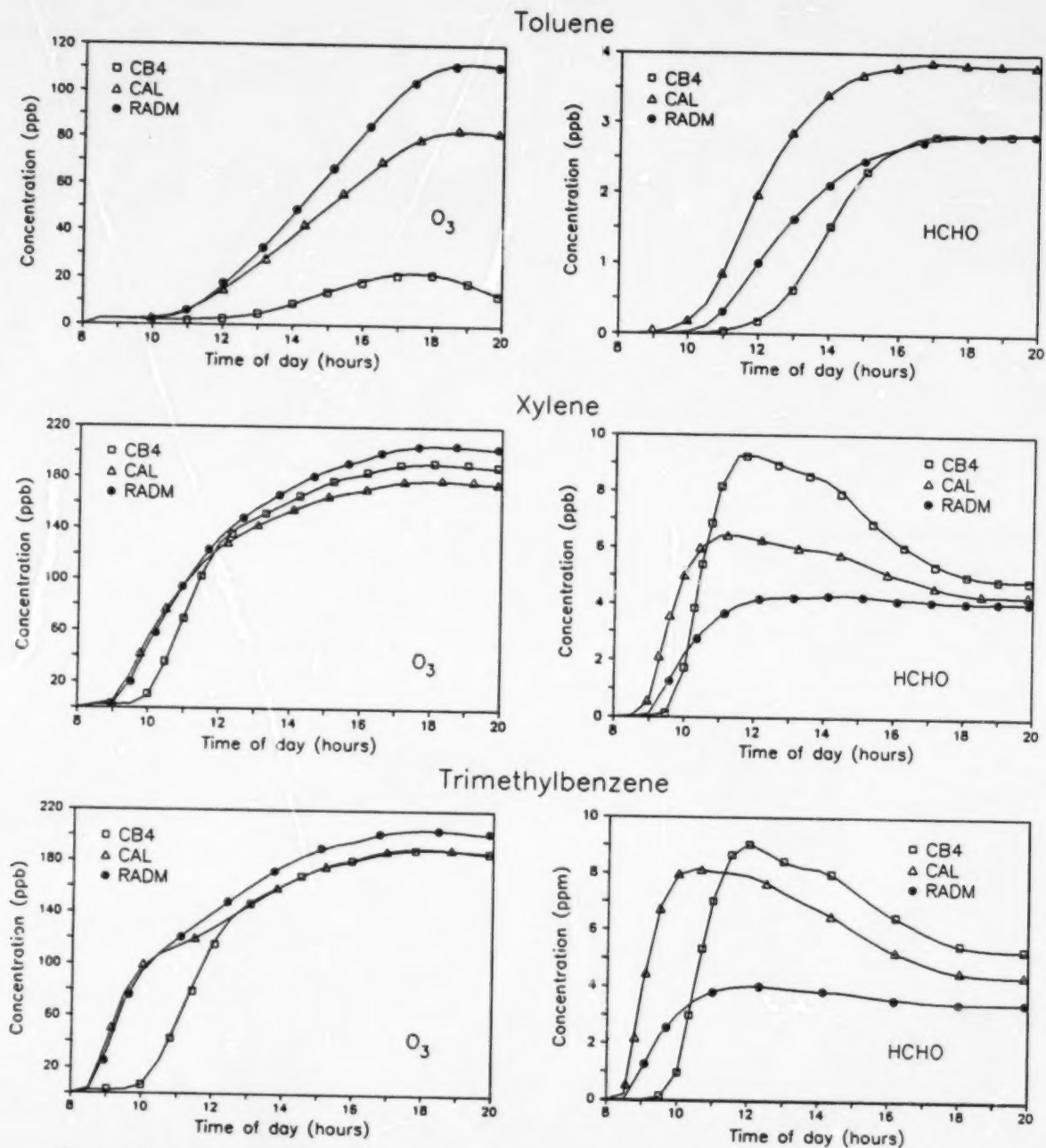


Fig. 5. Predicted oxidant concentrations as a function of time for the aromatic hydrocarbon simulations; VOC/NO_x = 9:1.

by a factor of 2 for a VOC/NO_x ratio of 18:1. The results are presented in Table 8. In general, the agreement among the mechanisms at the low and high VOC/NO_x ratios is comparable to the agreement noted in Table 7 for the simulations conducted at the medium ratio. That is, the mechanism that predicted the highest HCHO concentration for a particular organic at a ratio of 9:1 usually predicted the highest concentration at the other two ratios. The relative difference in predictions among the three mechanisms was also comparable for most of the organic species. Note, however, that the differences among the mechanisms for *trans*-2-butene and acetaldehyde increased significantly as the VOC/NO_x ratio

was increased. In the case of *trans*-2-butene, the RADM predicted significantly higher yields of HCHO at a VOC/NO_x ratio of 18:1 than the other two mechanisms. In the case of acetaldehyde, the CB4 predicted higher levels of HCHO than the CAL and RADM.

The large discrepancy noted for *trans*-2-butene at the high VOC/NO_x ratio is largely due to the fact that in the RADM, the reaction of OH with the generalized species used to represent the 2-alkenes and dienes includes HCHO as a reaction product. In contrast, the only means for producing HCHO from the 2-alkene surrogates used in the CB4 and CAL is through oxidation of acetaldehyde. The peroxyacetyl radicals

TABLE 8. Comparison of Maximum HCHO Concentrations Obtained for Selected VOC Species at Low and High VOC/NO_x Ratios

Organic	4.5:1				18:1			
	CB4	CAL	RADM	Δ, %	CB4	CAL	RADM	Δ, %
Ethene	27	29	30	10	121	118	125	6
Propene	27	26	26	4	103	92	94	11
<i>trans</i> -2-Butene	18	15	16	18	54	39	70	57
Acetaldehyde	18	17	17	6	54	42	38	36
Trimethylbenzene	6	7	4	50	17	19	11	50
Xylene	7	5	4	60	19	14	10	64
Toluene	1	2	2	50	7	7	5	33
Alkane mix	<1	<1	<1	—	<1	<1	<1	—
Urban mix ^b	3.9	4.3	3.8	12	16	16	15	6

Concentrations are in ppb; [NO_x]₀ = 0.06 ppm.

^aDifference between the highest and the lowest maximum concentration relative to the mean.

^bNo initial aldehydes.

formed during acetaldehyde oxidation produce HCHO when they react with NO. As the VOC/NO_x ratio increases, the fraction of acetaldehyde that can be oxidized to HCHO decreases because NO is rapidly depleted from the system. Consequently, at high ratios the CB4 and CAL tend to produce less HCHO than the RADM.

The other major difference noted in Table 8 concerns acetaldehyde where the CB4 predicted higher levels of HCHO at a VOC/NO_x ratio of 18:1 than did the other mechanisms. The CB4 also tended to produce somewhat higher HCHO levels at the 9:1 ratio and under those conditions, the differences resulted from the different rate constants used in the mechanisms to describe the formation of PAN. In this case, however, the differences cannot be explained by this reaction. The discrepancies noted for HCHO are largely caused by the different treatment of termination reactions for CH₃CO₃ radicals. All three mechanisms include the reaction of CH₃CO₃ with itself and with HO₂ radicals. The CB4 and CAL assume that HCHO is produced in both of these radical-radical reactions although the yield of HCHO for the self reaction and the rate constant for the CH₃CO₃ + HO₂ reaction are a factor of 2 lower in the CAL than in the CB4. In the RADM, formaldehyde is not included as a product of either reaction. The products included in the RADM for these reactions cannot further react to produce HCHO unless NO is available; radical-radical reactions, however, do not occur to any significant extent until NO has been depleted from the system. Thus, the products included in the RADM for these termination reactions are not expected to generate HCHO.

The representation of these reactions in the CB4 and CAL is different from that used in the RADM largely because of the desire on the part of the CB4 and CAL developers to limit the number of species included in their mechanisms. As an example, the expected products of the CH₃CO₃ self reaction are CH₃O₂ radicals. These radicals are not treated explicitly in the CB4 and CAL. Instead, they have been replaced with HCHO and HO₂, which are the products that most likely would result if CH₃O₂ were to react with NO. This approximation appears to have little effect on O₃ predictions obtained with the CB4 and CAL even under low NO_x conditions; the effect of this approximation on HCHO predictions, however, had not been tested.

A sensitivity study was conducted to determine the effect of the different assumptions used for these radical-radical reactions. In this study, it was assumed for all three mechanisms

that the reactions of CH₃CO₃ with itself and with HO₂ generate products that cannot further react to produce HCHO. When this change was made, HCHO yields obtained with the CB4, CAL and RADM mechanisms for the acetaldehyde simulation decreased from 54, 42, and 38 ppb to 43, 39, and 38 ppb, a mean difference of only 12% compared to the 36% indicated in Table 8. The different treatment of these radical-radical reactions also explains most of the discrepancy noted for propene at the high VOC/NO_x ratio since CH₃CO₃ is also a major product of propene oxidation. The different chemistry, however, had almost no effect on predictions obtained with the urban mix; HCHO predictions changed by less than 2% when the chemistry for the radical-radical reactions was altered and the urban mix simulations conducted at a VOC/NO_x ratio of 18:1 were repeated.

Effect of Reducing VOCs on HCHO Production in an Urban Mix

It is well known that ozone formation in photochemical systems is highly nonlinear with respect to VOC and NO_x [U.S. Environmental Protection Agency, 1986]. For example, decreasing VOC by a factor of 2 usually does not lead to a factor of 2 decrease in O₃. The results presented in Tables 7 and 8 suggest that formaldehyde production may not exhibit as strong a nonlinearity. Note in Table 8 that a factor of 4 decrease in [VOC]₀ for the urban mix simulation resulted in a factor of 4 decrease in HCHO yields for all three mechanisms. For example, at a VOC/NO_x ratio of 18:1, the CB4 yielded 16 ppb HCHO; at a ratio of 4.5:1, the CB4 produced 3.9 ppb HCHO. This near-linearity of HCHO production is better demonstrated in Table 9 where the mean HCHO concentration obtained with the three mechanisms for each VOC species has been normalized to an initial VOC concentration of 1 ppm C. If HCHO production were linear with respect to VOC, the HCHO yields reported for each organic in Table 9 should be identical at all three VOC/NO_x ratios. Note that the agreement is good in most cases. With the exception of acetaldehyde, trimethylbenzene, and xylene, HCHO yields at all three ratios agree to within 20% or better for each of the individual organic species and for the urban mix.

To further investigate the linearity of HCHO production, a series of simulations were conducted where the total VOC concentration of the initial mix was reduced by 2% through the control of selected classes of organics. The reduction of [VOC]₀ was limited to 2% because several classes of organics, such as the 2-alkenes, constitute very small percentages of the initial

TABLE 9. Mean Simulated Formaldehyde Yields for the Three Mechanisms as a Function of the VOC/NO_x Ratio

Organic	ppb [HCHO] _{max} / ppm C [VOC] _i		
	4.5:1	9:1	18:1
Ethene	107	120	112
Propene	96	94	89
<i>trans</i> -2-Butene	59	54	50
Acetaldehyde	63	52	42
Trimethylbenzene	21	13	15
Xylene	19	11	13
Toluene	7	6	6
Alkane mix	<1	<1	<1
Urban mix	15	16	15

mix. In these simulations, the rate constants used for the generalized species in the RADM mechanism were not altered as they were for the simulations of the individual organics. The urban mix used in these comparisons is the one presented in

Table 7 that contained no initial aldehydes. The results obtained at a VOC/NO_x ratio of 9:1 are reported in Table 10. The first two columns of data compare the reduction in the simulated HCHO yield to the reduction that would be expected if the organics generated the same level of HCHO in the mix that they did when simulated individually. For example, according to Table 7, the CB4 simulation of the ethene-only mix generated 62 ppb HCHO. If HCHO production is linear, a 2% reduction in [VOC]_i achieved through control of ethene should lower the HCHO yield by (0.02)(62) or 1.24 ppb, which is a decrease of 13.9% from the simulated yield of 8.9 ppb reported in Table 7 for the CB4. Note that the calculated percent reduction in HCHO for this case was greater than the simulated reduction. Consequently, reducing ethene in the urban mix had somewhat less of a benefit on HCHO levels than expected based on the behavior of this organic in the ethene-only mix.

Reductions in the other olefins and the monoalkylbenzenes led to simulated decreases in HCHO that were very close to the calculated decreases. A reduction in the di- and trialkyl-

TABLE 10. Effect of Reducing Selected Organics on Predictions Obtained at a VOC/NO_x Ratio of 9:1

Organic Reduced	Mechanism	Percent Decrease in Maximum Concentration			
		(HCHO) _{sim}	(HCHO) _{calc}	(O ₃) _{sim}	(H ₂ O ₂) _{sim}
Ethene	CB4	12.2	13.9	8.7	43
	CAL	12.3	14.7	7.7	47
	RADM	<u>13.4</u>	<u>16.4</u>	<u>8.1</u>	<u>41</u>
	Mean	12.6	15.0	8.2	44
1-Alkenes ^a	CB4	11.8	7.0	12.2	53
	CAL	10.0	10.0	8.5	47
	RADM	<u>10.3</u>	<u>12.5</u>	<u>8.9</u>	<u>45</u>
	Mean	10.7	9.8	9.9	48
2-Alkenes	CB4	7.5	4.7	10.4	45
	CAL	5.9	4.2	8.5	50
	RADM	<u>6.1</u>	<u>8.3</u>	<u>11.1</u>	<u>52</u>
	Mean	6.5	5.7	10.0	49
Trialkylbenzenes	CB4	4.3	1.6	7.8	41
	CAL	4.4	1.7	10.6	56
	RADM	<u>2.9</u>	<u>1.0</u>	<u>8.9</u>	<u>45</u>
	Mean	3.9	1.4	9.1	47
Dialkylbenzenes	CB4	4.4	1.8	8.7	43
	CAL	2.7	1.3	7.0	44
	RADM	<u>2.9</u>	<u>1.0</u>	<u>8.9</u>	<u>45</u>
	Mean	3.3	1.4	8.2	44
Monoalkylbenzenes	CB4	1.2	0.6	1.7	14
	CAL	0.6	0.8	2.1	19
	RADM	<u>0.7</u>	<u>0.7</u>	<u>3.7</u>	<u>18</u>
	Mean	0.8	0.7	2.5	17
Alkanes	CB4	0.7	0.02	0.5	0
	CAL	0.2	0.06	0.7	3
	RADM	<u>0.4</u>	<u>0.03</u>	<u>0.7</u>	<u>0</u>
	Mean	0.4	0.04	0.6	1
All VOC Species	CB4	2.7	2.0	3.4	17
	CAL	1.8	2.0	2.8	19
	RADM	<u>2.0</u>	<u>2.0</u>	<u>3.7</u>	<u>18</u>
	Mean	2.2	2.0	3.3	18

In all simulations [VOC]_i was reduced by 2% from its basecase value of 0.54 ppm C. The calculated percent decreases in HCHO were derived from the HCHO yields reported in Table 7 for the individual organic species.

^aExcluding ethene.

benzenes, however, led to decreases in HCHO yields that exceeded the calculated decreases by more than a factor of 2. Thus, although these aromatics generate very low levels of HCHO, reducing these highly reactive organics apparently lowers the reactivity of the mix to such an extent that the HCHO-forming potential of the remaining VOCs is reduced.

A reduction in alkanes led to a simulated mean decrease in HCHO that exceeded the calculated decrease by a factor of 10. Thus, when part of an urban mix, alkanes generate substantially more HCHO than they do in a mix containing only alkanes. Due to its low reactivity, an alkane-only mix is unable to generate enough free radicals to effect much oxidation. In an urban mix, however, the reactive alkenes and aromatics generate sufficient free radicals to oxidize a larger portion of the alkanes.

The decreases in HCHO yields obtained for reductions in ethene and the other 1-alkenes far exceeded the decreases noted when any of the other organics were reduced. A simulation was also conducted where all the 1-alkenes, including ethene, were removed from the VOC mix. The mean decrease in HCHO levels obtained for the three mechanisms was 55% although [VOC]_i in this test case was only reduced by 10%. Thus, although the 1-alkenes constitute a small portion of the urban mix, they appear to be responsible for more than 50% of the formaldehyde that is produced.

Note in Table 10 that when all organics in the urban mix were uniformly reduced, the simulated HCHO yields for all but the CB4 mechanism were very close to the yields that would be expected if HCHO production were linear. If this finding is applicable to the urban environment, it suggests that a given percent reduction in VOC may lead to a comparable percent reduction in peak HCHO levels.

Also included in Table 10 are the percent reductions in O₃ and H₂O₂ that resulted from control of the various organics. The decreases noted for H₂O₂ were large in many cases (>40%); however, little significance should be attached to these numbers because H₂O₂ concentrations tended to be very low in these simulations. (As indicated in Table 7, the mean H₂O₂ concentration obtained with the three mechanisms prior to VOC control was only 0.2 ppb.)

Note in Table 10 that with the exception of the monoalkylbenzenes and the alkanes, which are inefficient oxidant producers, the simulated decreases in O₃ and H₂O₂ yields were not greatly affected by the nature of the organics that were controlled. Excluding these two classes of organics, the decreases in O₃ varied by only a factor of 1.2 (from a high of 10.0% to a low of 8.2%). The decreases noted for H₂O₂ showed even less variability. Note, however, that the simulated decreases in HCHO for these five classes of organics ranged from 12.6 to 3.3%, which is a difference of almost a factor of 4. Consequently, strategies to limit HCHO production appear to depend more critically on the nature of the organic species that is controlled than do strategies to limit O₃ or H₂O₂ formation.

The simulations presented in Table 10 were also conducted at VOC/NO_x ratios of 4.5:1 and 18:1. The results obtained for HCHO and O₃ at all three ratios are compared in Table 11. Note that control of ethene is predicted to have a somewhat greater effect on HCHO formation at the high VOC/NO_x ratio while the greatest percent reductions in HCHO concentrations for all other classes of organics occurred at the low VOC/NO_x ratio. Note also that at a VOC/NO_x ratio of 18:1, the relative rankings of the organics in terms of limiting HCHO production is the same as the ranking for limiting O₃ formation. That is,

TABLE 11. Comparison of the Effect of Reducing Selected Organics as a Function of the VOC/NO_x Ratio

Organic Reduced	Mean Reduction in Maximum Concentration, %					
	Formaldehyde			Ozone		
	4.5:1	9:1	18:1	4.5:1	9:1	18:1
Ethene	10.6	12.6	13.7	5.2	8.2	2.2
1-Alkenes ^a	11.3	10.7	9.9	7.6	9.9	1.7
2-Alkenes	8.1	6.5	4.4	8.2	10.0	1.4
Trialkylbenzenes	5.1	3.9	1.7	7.2	9.1	0.8
Dialkylbenzenes	4.3	3.3	1.3	6.0	8.2	0.6
Monoalkylbenzenes	0.9	0.8	0.3	1.4	2.5	0.3
Alkanes	0.4	0.4	0.2	0.5	0.6	0.2
All VOC species	2.3	2.2	1.6	2.3	3.3	0.5

^aExcluding ethene.

control of the organic class that led to the greatest reduction in HCHO also led to the greatest reduction in O₃. This is not the case at the other VOC/NO_x ratios. At a ratio of 4.5:1, reductions in the 1-alkenes led to the largest decrease in HCHO whereas reduction in the 2-alkenes led to the largest decrease in O₃. At a VOC/NO_x ratio of 9:1, reductions in ethene led to the greatest decrease in HCHO whereas reductions in the non-ethene alkenes led to the greatest decreases in O₃. Thus, optimum control strategies for limiting HCHO formation in the urban environment might not necessarily be the optimum strategies for limiting O₃ production.

CONCLUSIONS

In simulations conducted with a typical urban pollutant mix, the CB4, CAL and RADM mechanisms were found to yield very comparable predictions for formaldehyde provided that the same rates were used in all three mechanisms to describe the photolysis of HCHO. The good agreement obtained was somewhat surprising since the mechanisms have largely been optimized to reproduce O₃ profiles observed in smog chamber studies. Considerably less attention has been paid to achieving good agreement to the HCHO yields obtained in these experiments.

The close agreement for HCHO in the urban mix simulations was largely due to the fact that the three mechanisms yield very similar predictions for ethene and the other 1-alkenes. These species were responsible for more than 50% of the HCHO produced in the urban mix simulations. Significant discrepancies were noted for formaldehyde predictions obtained for VOC mixtures that contained only aromatics or alkanes. These species, however, contribute substantially less to HCHO production than the 1-alkenes. Consequently, their presence in the urban mix had only a minor impact on HCHO predictions.

When different rates were used to describe the photolysis of HCHO, the agreement among the mechanisms for the urban mix simulations was not as good. Formaldehyde predictions differed by as much as 20% depending on whether the Bass *et al.* [1980] or the Moortgat *et al.* [1980] cross sections were used to derive HCHO photolysis rates; predictions of H₂O₂ varied by as much as 50%. Better characterization of absorption cross sections for HCHO is needed before production of HCHO and H₂O₂ in the urban environment can be simulated reliably.

Predictions of O₃ and H₂O₂ were found to be very sensitive to assumptions made about the aldehyde content of the initial VOC mix. Until aldehyde emissions are adequately character-

ized, the accuracy of O_3 and H_2O_2 predictions obtained with atmospheric models will be in doubt.

In simulations where acetaldehyde was a major reaction product, uncertainties in the rate constant for reaction of peroxyacetyl radicals with NO_2 were found to have an impact on predictions of HCHO and other oxidants. Uncertainties in our understanding of the chemistry of aromatic VOCs also had a substantial impact on predictions. Much of the difference in O_3 and H_2O_2 yields noted for the urban mix simulations could be explained by differences in the treatment of aromatic VOC chemistry. It was found, however, that altering the chemistry of aromatic hydrocarbons to improve the agreement in O_3 and H_2O_2 predictions tended to cause the mechanisms to show more of a discrepancy in their predictions for HCHO.

In the simulation of an acetaldehyde-only mix, it was found that assumptions invoked by several of the mechanism developers to limit the number of organic free radical species contained in the mechanisms had a substantial impact on HCHO levels obtained at high VOC/ NO_2 ratios. These assumptions, though, had almost no effect on HCHO predictions for a typical urban mix of organic pollutants. There may, however, be other assumptions made by the mechanism developers that could limit the ability of the mechanisms to yield accurate HCHO predictions under typical urban conditions. Mechanism developers, when deciding on the level of detail to include in their mechanisms, normally conduct sensitivity studies to assure themselves that the condensation techniques do not compromise results obtained for many of the important oxidant-forming parameters, such as the rate of oxidation of NO to NO_2 or the rate of production of ozone. Considerably less attention has been devoted to insuring that the approximations are adequate for predicting HCHO formation. For example, it may be appropriate to represent dienes as *trans*-2-butene, as done in the CAL mechanism, if predictions of O_3 are the only concern. Likewise, it is probably valid when simulating O_3 to represent a molecule of *trans*-2-butene as two molecules of acetaldehyde as done in the CB4. These approximations, however, may not be appropriate for predicting HCHO formation in the urban environment. A more extensive smog chamber data base of HCHO production from VOC- NO_2 mixtures and a more complete evaluation of the mechanisms against this data base will be needed before the reliability of HCHO predictions obtained with existing oxidant models can be fully assessed.

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